(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 798 127 A1

# (12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
**01.10.1997 Bulletin 1997/40**

(51) Int. Cl.[6]: **B41M 5/30**

(21) Application number: **97105273.3**

(22) Date of filing: **27.03.1997**

(84) Designated Contracting States:
**DE GB**

(30) Priority: **28.03.1996 JP 103424/96**

(71) Applicants:
- **Oji Paper Co., Ltd.**
  **Tokyo-to (JP)**
- **SANKO KAIHATSU KAGAKU KENKYUSHO CORPORATION**
  **Ibaraki-shi Osaka-fu (JP)**

(72) Inventors:
- **Inatsu, Naoko**
  **Amagasaki-shi, Hyogo-ken (JP)**
- **Furukawa, Hiroyuki**
  **Amagasaki-shi, Hyogo-ken (JP)**
- **Tsuchida, Tetsuo**
  **Takarazuka-shi, Hyogo-ken (JP)**
- **Saito, Toranosuke**
  **Ibaraki-shi, Osaka-fu (JP)**
- **Ishibashi, Takashi**
  **Ibaraki-shi, Osaka-fu (JP)**

(74) Representative: **Barz, Peter, Dr.**
**Patentanwalt**
**Kaiserplatz 2**
**80803 München (DE)**

## (54) Heat sensitive recording material and method of using it

(57) The present invention provides a heat sensitive recording material comprising a recording layer formed on a substrate and containing a colorless or light-colored basic dye and a color acceptor, the material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in the recording layer, and a method of using the heat sensitive recording material.

EP 0 798 127 A1

Printed by Rank Xerox (UK) Business Services
2.14.14/3.4

## Description

The present invention relates to heat sensitive recording materials, and more particularly to heat sensitive recording materials which are least likely to become impaired in whiteness and excellent in the preservability of recorded images in high-temperature environments, and a method of using the same.

Heat sensitive recording materials are well known which utilize the reaction between a colorless or light-colored basic dye and a color acceptor for producing recorded images by thermally reacting the two chromogenic substances. Such recording materials are relatively inexpensive, are usable with a recording device which is compact and free of maintenance and are therefore in use in a wide variety of fields.

For example, with the POS (Point of Sales) label system placed into production processes, a heat sensitive recording material is sometimes used in a printer placed in high-temperature environments of 80 °C or higher. Alternately, a heat sensitive recording material is in some cases placed in high-temperature circumstances of 80 °C or higher after recording. It is desired to provide heat sensitive recording materials which are usable free of background fogging even at an ambient temperature of 80 °C or higher and outstanding in the preservability of recorded images.

Although the sensitizer heretofore generally used improves the recording sensitivity, it accompanies the drawback of causing background fogging at such high-temperature environments. Thus satisfactory results still remain to be achieved.

Accordingly, it is strongly desired to provide a heat sensitive recording material which is excellent in the recording sensitivity, and has a recording layer which does not permit its blank portion (background area) to become impaired in whiteness even when the material is used or stored under high-temperature conditions, the material further being capable of retaining recorded images with good stability.

An object of the present invention is to provide a heat sensitive recording material which is least likely to produce background fogging even when used or stored under high-temperature environments and excellent in the preservability of recorded images, and a method of using the same.

The above and other objects of the invention will become apparent from the following description.

The present invention provides a heat sensitive recording material comprising a recording layer formed on a substrate and containing a colorless or light-colored basic dye and a color acceptor, the material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in the recording layer.

Further, the invention provides a method of using a heat sensitive recording material which is used or stored at high-temperature circumstances, the heat sensitive recording material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in a recording layer.

In a heat sensitive recording material comprising a recording layer formed on a substrate and containing a colorless or light-colored basic dye and a color acceptor, the present invention provides a heat sensitive recording material which is least likely to produce background logging even when exposed to high-temperature environments and excellent in the preservability of recorded images, by incorporating 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane in the recording layer.

1-Phenoxy-2-(2-naphthoxy)ethane and 1,3-bis(2-naphthoxy)propane used in the invention are employed in the heat sensitive recording material disclosed for example in JP-B-33,630/1992 and USP 4,531,140. However, these compounds are used in order to enhance the recording sensitivity of the heat sensitive recording material in the references. It is nothing disclosed or suggested in the references that the compounds are effective to provide a heat sensitive recording material which is free of background logging even at high-temperature and excellent in the preservability of recorded images, and a method of use thereof. In the present invention, a heat sensitive recording material can be obtained which is least likely to produce background logging even when used or stored under high-temperature environments of more than 80 °C and excellent in the preservability of recorded images, by using the above specific heat-fusible substance (sensitizer). The upper temperature in which the above effect is attained depends on the kind and ratio to be used of the basic dye, color acceptor and heat-fusible substance and is not defined specifically but the effect is obtained up to about 120 °C .

It is desired that the amount of 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane be adjusted generally within the range of 10 to 700 parts by weight, preferably about 50 to about 500 parts by weight, per 100 parts by weight of the basic dye although not limited specifically.

Various known dyes are usable as the colorless or light-colored basic dye which is the component of the recording layer of the present heat sensitive recording material. Examples thereof are as follows.

3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran,
3-diethylamino-7-(m-trifluoromethylanilino)fluoran,
3-(N-ethyl-N-isoamylamino)-7-(o-chloroanilino)fluoran,
3-di-n-pentylamino-6-methyl-7-anilinofluoran,
3-[N-(3-ethoxypropyl)-N-ethylamino]-6-methyl-7-anilinofluoran,
3-[N-(3-ethoxypropyl)-N-methylamino]-6-methyl-7-anilinofluoran,

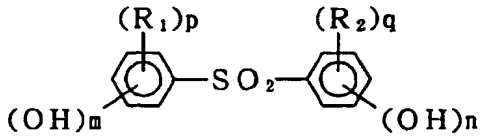
3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran,
3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran,
3-diethylamino-6-methyl-7-anilinofluoran,
3-di-n-butylamino-6-methyl-7-anilinofluoran,
3-diethylamino-6-methyl-7-(2,4-xylylidino)fluoran,
3-diethylamino-7-(o-chloroanilino)fluoran,
3-di-n-butylamino-7-(o-chloroanilino)fluoran,
3-di-n-butylamino-7-(o-fluoroanilino)fluoran,
3-(N-ethyl-N-cyclopentylamino)-6-methyl-7-anilinofluoran,
3-diethylamino-6-chloro-7-anilinofluoran,
3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluoran,
3-pyrrolidino-6-methyl-7-anilinofluoran,
3-diethylamino-6-methyl-7-(2,6-xylylidino)fluoran,
3-(N-methyl-N-n-propylamino)-6-methyl-7-anilinofluoran,
2,2-bis{4-[6'-(N-cyclohexyl-N-methylamino)-3'-methylspiro(phthalide-3,9'-xanthene)-2'-ylamino]phenyl}propane,
3-diethylamino-6-methyl-7-chlorofluoran,
3-diethylamino-7-chlorofluoran,
3-diethylamino-6,7-dimethylfluoran,
3,3'-bis(1-ethyl-2-methylindole-3-yl)phthalide,
3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide,
3-(4-diethylamino-2-methylphenyl)-3-(4-dimethylaminophenyl)-6-dimethylaminophthalide,
3,7-bis(dimethylamino)-10-benzoylphenotiazine,
3,3-bis[1-(4-methoxyphenyl)-1-(4-dimethylaminophenyl)ethylene-2-yl]-4,5,6,7-tetrachlorophthalide,
3,3'-bis(4-diethylamino-2-ethoxyphenyl)-4-azaphthalide,
3-di-n-pentylamino-6,8,8-trimethyl-9-ethyl-8,9-dihydro(3,2,e)pyridofluoran,
3-di-n-butylamino-6,8,8-trimethyl-9-ethyl-8,9-dihydro(3,2,e)pyridofluoran,
3-[1,1-bis(4-diethylaminophenyl)ethylene-2-yl]-6-dimethylaminophthalide,
3-(4-dimethylaminophenyl)amino-5,7-dimethylfluoran,
3-(4-dibutylaminophenyl)amino-6-methyl-7-chlorofluoran,
3-(1-methyl-2-phenylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide and 3-(1-methyl-2-phenylindole-3-yl)-3-(2-methyl-4-diethylaminophenyl)-4,7- diazaphthalide. Of course the dyes are not limited to thereabove and are used in a mixture of at least two of them as required.

Among the above dyes, especially preferably used are 3-di-n-butylamino-6-methyl-7-anilinofluoran, 3-di-n-pentylamino-6-methyl-7-anilinofluoran, 3-di-n-butylamino-7-(o-chloroanilino)fluoran and 3-diethylamino-7-(m-trifluoromethylanilino)fluoran which exhibit excellent color forming ability and are free of background fogging.

Various known compounds are usable as the color acceptor which is the component of the heat sensitive recording layer. Examples thereof are as follows.

2,2-Bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, bis(4-hydroxyphenylthioethoxy)methane, 1,4-bis[α-methyl-α-(4'-hydroxyphenyl)ethyl]benzene, 1,3-bis[α-methyl-α-(4'-hydroxyphenyl)ethyl]benzene, 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, bis(3-allyl-4-hydroxyphenyl)sulfone, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 1-[α-methyl-α-(4-hydroxyphenyl)ethyl]-4-[α',α'-bis(4-hydroxyphenyl)ethyl]benzene, benzyl 4-hydroxybenzoate, butyl bis(4-hydroxyphenyl)acetate, bis(4-hydroxyphenylthioethyl) ether, N-(p-tolylsulfonyl)-N'-phenylurea, 4,4'-bis(p-toluenesulfonylaminocarhonylamino)diphenylmethane, zinc salt of 4-[2-(p-methoxyphenoxy)ethoxy]salicylic acid, zinc salt of 4-[3-(p-tolylsulfonyl)propyloxy]salicylic acid, zinc salt of 5-[p-(2-p-methoxyphenoxyethoxy)cumyl]salicylic acid, zinc salt of 4-octyloxyacetylaminosalicylic acid, and complex of antipyrine and zinc thiocyanate. The color acceptors are used in a mixture of at least two of them as required.

Preferable among these color acceptors are diphenylsulfone derivatives represented by the following formula (1), since such derivatives afford a heat sensitive recording material which is least likely to become impaired in whiteness and excellent in the preservability of recorded images in high-temperature environments.



(1)

wherein $R_1$ and $R_2$ are each $C_1$~$C_4$ alkyl, $C_2$~$C_4$ alkenyl, $C_1$~$C_4$ alkoxyl, benzyloxy or halogen atom, m is an integer of 0 to 2, n is an integer of 1 to 3, p and q are each an integer of 0 to 2.

Preferable among the diphenylsulfone derivatives of the formula (1) are bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone and 2,4'-dihydroxydiphenylsulfone, since such compounds afford a heat sensitive recording material which is least likely to become impaired in whiteness and excellent in preservability of recorded images in high-temperature environments.

It is desired that the ratio of the color acceptor to the basic dye to be used therewith he adjusted generally within the range of 100 to 700 parts by weight, preferably about 150 to about 400 parts by weight, per 100 parts by weight of the basic dye although not limited specifically.

In the present heat sensitive recording material, it is possible to incorporate various known heat-fusible substances into the recording layer in order to improve record sensitivity insofar as these substance are not detrimental to the contemplated effect of the present invention.

Examples of useful heat-fusible substances are stearic acid amide, stearic acid ethylenebisamide, stearic acid methylenebisamide, stearic acid N-methylolamide, dibenzyl terephthalate, dimethyl terephthalate, benzyl p-benzyloxybenzoate, 1-hydroxy-2-naphthoic acid phenyl ester, oxalic acid di-p-chlorobenzyl ester, oxalic acid di-p-methylbenzyl ester, 2-naphthyl benzyl ether, p-benzylbiphenyl, biphenyl p-tolyl ether, bis(4-methoxyphenoxy) ether and 1,4-bis(vinyloxyethoxy)benzene.

It is further possible to incorporate various known preservability improving agent into the recording layer in order to improve recorded image preservability.

Examples of useful preservability improving agents are 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 2-(2-hydroxy-5-methylphenyl)benzotriazole, tetrakis(1,2,2,6,6-pentamethyl-4-piperidinyl)-1,2,3,4-butanetetracarboxylate, 4-benzyloxyphenyl-4'-(2-methyl-2,3-epoxypropyloxy)phenylsulfone, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 4,4'-butylidenebis(6-tert-butyl-m-cresol), bis[2-hydroxy-3-(2'H-benzotriazole-2'-yl)-5-octylphenyl]methane and sodium salt or magnesium salt of 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphoric acid.

A coating composition is prepared from these components, for example, by dispersing the dye, color acceptor, heat-fusible substance and the like into a dispersion medium which is generally water, at the same time or individually, with use of a stirring-pulverizing machine such as a ball mill, attritor, sand mill or colloid mill.

Usually a hinder is incorporated into the coating composition in an amount of 2 to 40 wt.% , preferably about 5 to about 25 wt.% , based on the total solids content of the composition. Examples of useful hinders are starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, gum arabic, polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, sulfo-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, silicon-modified polyvinyl alcohol and like modified polyvinyl alcohols, styrene-maleic anhydride copolymer salt, styrene-acrylic acid copolymer salt, styrene-butadiene copolymer emulsion, etc. At least two of these hinders can of course be used in combination.

Various auxiliary agents can further be added to the coating composition. Examples of useful agents are dispersants such as sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl alcohol sulfuric acid ester and metal salts of fatty acids, ultraviolet absorbers of the triazoles and like types, and other agents including defoaming agents, fluorescent dyes, coloring dyes and antioxidants.

To prevent the heat sensitive recording material from sticking to the recording device or recording head on contact therewith, it is possible to add to the coating composition a dispersion or emulsion of stearic acid, polyethylene wax, carnauba wax, paraffin wax, zinc stearate, calcium stearate, ester wax or the like.

To diminish the adhesion of tailings to the recording head, it is also possible to add to the coating composition an inorganic pigment such as kaolin, clay, talc, calcium carbonate, calcined clay, titanium oxide, kieselguhr, finely divided anhydrous silica or activated clay, and organic pigment such as urea-formaldehyde resin filler.

Examples of useful substrates are paper (including also acidic paper and neutralized paper), plastic film, synthetic paper, sheets prepared by affixing a plastic film or synthetic paper to coated paper, wood-free paper or the like with an adhesive, and sheets obtained by laminating a plastic to paper.

Examples of useful plastic films are those of polyethylene, polyester, polypropylene, polyvinyl chloride, polystyrene and nylon. Examples of useful synthetic papers are those prepared by film methods or the fiber method. The film meth-

ods include the internal paper making method wherein a synthetic resin, filler and additives are melted and kneaded, and the resulting mixture is extruded into a film, the surfac coating method wherein a pigment coating layer is formed, and the surafce treating method. Synthetic papers obtained by the fiber method include synthetic pulp paper and spun bonded paper.

With the heat sensitive recording material of the invention, the method of forming the recording layer is not limited specifically. The recording layer can be formed by known conventional techniques, for example, by applying a coating composition for forming this layer to a substrate with suitable means, such as bar coating, air knife coating, rod blade coating, pure blade coating, short dwell coating or curtain coating, and drying the resulting coating. In case of using a plastic film as the substrate, it is possible to enhance coating efficiency by subjecting the surface to corona discharge treatment, electron rays irradiation or the like. The amount of coating composition to be applied, which is not limited particularly, is usually 2 to 10 g/m$^2$, preferably 3 to 7 g/m$^2$, based on dry weight.

Further, it is possible to obtain a heat sensitive recording material having excellent printability, amenability to cinnabar seal ink, writability and the like by providing on the heat sensitive recording layer a protective layer which is constituted by an adhesive, lubricant, pigment or the like.

Examples of adhesives usable in the protective layer are polyvinyl alcohol having various saponification degrees, acetoacetyl-modified polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, silicone-modified polyvinyl alcohol, acrylic resin, polyurethane resin, etc. The adhesive can be used in an amount of 10 to 95 % by weight, preferably 30 to 90 % by weight based on the total solids of the protective layer. The protective layer is coated in an amount of 0.5 to 10 g/m$^2$, preferably 1 to 7 g/m$^2$, based on dry weight.

Various other known techniques in the field of heat sensitive recording materials can be applied. For example, it is possible to form on the protective layer a layer comprising a water-soluble, water-dispersible, electron ray-curable or ultraviolet ray-curable resin in order to provide excellent gloss, to form a protective layer on the rear surface of the substrate, to form an undercoat layer on the surface of the substrate.

The present invention will he described in greater detail with reference to the following examples, to which the invention is not limited. The parts and percentages in these examples are by weight unless otherwise specified.

Example 1

(1) Formation of undercoat layer

A coating composition for an undercoat layer was prepared by mixing together 100 parts of calcined clay (Ansilex, product of Engelhard Corp.), 15 parts of styrene-butadiene copolymer latex (solids content: 50 %), 30 parts of 10 % aqueous solution of polyvinyl alcohol and 100 parts of water. The coating composition obtained was applied to wood-free paper, weighing 50 g/m$^2$, in an amount of 10 g/m$^2$ when dried, followed by drying to form an undercoat layer.

(2) Preparation of Composition A

A composition comprising 10 parts of 3-di-n-butylamino-6-methyl-7-anilinofluoran, 5 parts of 5 % aqueous solution of methyl cellulose and 15 parts of water was pulverized to a mean particle size of 1.0 μm by a sand mill.

(3) Preparation of Composition B

A composition composed of 15 parts of 1-phenoxy-2-(2-naphthoxy)ethane, 7 parts of 5 % aqueous solution of methyl cellulose and 28 parts of water was pulverized to a mean particle size of 1.5 μm by a sand mill.

(4) Preparation of Composition C

A composition composed of 20 parts of bis(3-allyl-4-hydroxyphenyl)sulfone, 10 parts of 5 % aqueous solution of methyl cellulose and 30 parts of water was pulverized to a mean particle size of 1.4 μm by a sand mill.

(5) Formation of heat sensitive recording layer

A coating composition for forming a heat sensitive recording layer was prepared by mixing together with stirring 30 parts of Composition A, 50 parts of Composition B, 60 parts of Composition C, 150 parts of 10 % aqueous solution of polyvinyl alcohol and 10 parts of calcium carbonate. The composition obtained was applied onto the above undercoat layer in an amount by dry weight of 4 g/m$^2$ and dried.

Example 2

A heat sensitive recording material was prepared in the same manner as in Example 1 except that in preparing Composition B, 1-phenoxy-2-(2-naphthoxy)ethane was replaced by 1,3-bis(2-naphthoxy)propane.

Examples 3 to 5

Heat sensitive recording materials were prepared in the same manner as in Example 1 except that in preparing Composition C, the following compounds were used in place of bis(3-allyl-4-hydroxyphenyl)sulfone.

Example 3; 4-hydroxy-4'-isopropoxydiphenylsulfone
Example 4; 2,4'-dihydroxydiphenylsulfone
Example 5; 1,1-bis(4-hydroxyphenyl)-1-phenylethane

Examples 6 to 7

Heat sensitive recording materials were prepared in the same manner as in Example 2 except that in preparing Composition C, the following compounds were used in place of bis(3-allyl-4-hydroxyphenyl)sulfone.

Example 6; 4-hydroxy-4'-isopropoxydiphenylsulfone
Example 7; 2,4'-dihydroxydiphenylsulfone

Examples 8 to 10

Heat sensitive recording materials were prepared in the same manner as in Example 1 except that in preparing Composition A, the following compounds were used in place of 3-di-n-butylamino-6-methyl-7-anilinofluoran.

Example 8; 3-di-n-pentylamino-6-methyl-7-anilinofluoran
Example 9; 3-di-n-butylamino-7-(o-chloroanilino)fluoran
Example 10; 3-diethylamino-7-(m-trifluoromethylanilino)fluoran

Examples 11 to 13

Heat sensitive recording materials were prepared in the same manner as in Example 2 except that in preparing Composition A, the following compounds were used in place of 3-di-n-butylamino-6-methyl-7-anilinofluoran.

Example 11; 3-di-n-pentylamino-6-methyl-7-anilinofluoran
Example 12; 3-di-n-butylamino-7-(o-chloroanilino)fluoran
Example 13; 3-diethylamino-7-(m-trifluoromethylanilino)fluoran

Comparative Examples 1 to 4

Heat sensitive recording materials were prepared in the same manner as in Example 1 except that in preparing Composition B, the following compounds were used in place of 1-phenoxy-2-(2-naphthoxy)ethane.

Comparative Example 1; 1,2-diphenoxyethane
Comparative Example 2; 1-phenoxy-2-(1-naphthoxy)ethane
Comparative Example 3; 1,2-bis(3-methylphenoxy)ethane
Comparative Example 4; 2-naphthyl benzyl ether

Images were recorded on the seventeen (17) kinds of heat sensitive recording materials thus obtained by a heat sensitive recording tester (Model TH-PMD, product of Ohkura Denki Co., Ltd., applied voltage 18 V, pulse cycle 3.0 ms, applied pulse width 2.0 ms), and then checked for the color density of recorded images and the background density of blank areas by a Macbeth densitometer (Model RD-914, product of Macbeth Corp.). Table 1 shows the results. The recording materials used for recording were allowed to stand in a hot air dryer at 90 °C for 3 hours and thereafter checked again for the color density of recorded images and the background density of blank areas. The results are also given in Table 1 as "after treatment".

Table 1

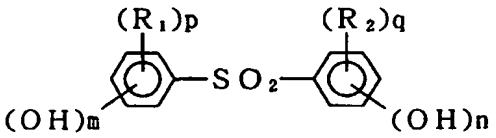
| | before treatment | | after treatment | |
|---|---|---|---|---|
| | color density | background density | color density | background density |
| Ex.1 | 1.45 | 0.05 | 1.24 | 0.10 |
| Ex.2 | 1.46 | 0.05 | 1.27 | 0.09 |
| Ex.3 | 1.45 | 0.05 | 1.24 | 0.11 |
| Ex.4 | 1.42 | 0.05 | 1.22 | 0.10 |
| Ex.5 | 1.35 | 0.05 | 1.13 | 0.09 |
| Ex.6 | 1.45 | 0.05 | 1.26 | 0.11 |
| Ex.7 | 1.43 | 0.05 | 1.23 | 0.09 |
| Ex.8 | 1.44 | 0.05 | 1.24 | 0.10 |
| Ex.9 | 1.44 | 0.05 | 1.20 | 0.08 |
| Ex.10 | 1.46 | 0.05 | 1.22 | 0.09 |
| Ex.11 | 1.45 | 0.05 | 1.26 | 0.09 |
| Ex.12 | 1.43 | 0.04 | 1.21 | 0.08 |
| Ex.13 | 1.43 | 0.04 | 1.24 | 0.08 |
| Com.Ex.1 | 1.46 | 0.06 | 0.97 | 0.36 |
| Com.Ex.2 | 1.41 | 0.06 | 0.94 | 0.28 |
| Com.Ex.3 | 1.44 | 0.05 | 1.09 | 0.25 |
| Com.Ex.4 | 1.40 | 0.06 | 1.05 | 0.30 |

The results given in Table 1 reveal that the heat sensitive recording materials of the present invention were very small in the reduction of whiteness and excellent in the preservability of recorded images in high-temperature environments. Thus, the present heat sensitive recording material is extremely suitable for use and store under high-temperature environments.

## Claims

1. A heat sensitive recording material comprising a recording layer formed on a substrate and containing a colorless or light-colored basic dye and a color acceptor, the material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in the recording layer.

2. A heat sensitive recording material as defined in claim 1 wherein the color acceptor is at least one of a diphenylsulfone derivative of the formula (1)




(1)

wherein $R_1$ and $R_2$ are each $C_1$~$C_4$ alkyl, $C_2$~$C_4$ alkenyl, $C_1$~$C_4$ alkoxyl, benzyloxy or halogen atom, m is an integer of 0 to 2, n is an integer of 1 to 3, p and q are each an integer of 0 to 2.

3. A heat sensitive recording material as defined in claim 2 wherein the color acceptor is bis(3-allyl-4-hydroxyphe-

nyl)sulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone or 2,4'-dihydroxydiphenylsulfone.

4. A method of recording the image on a heat sensitive recording material which is used or stored at a high temperature circumstance, the heat sensitive recording material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in a recording layer.

5. A method of using a heat sensitive recording material which is used or stored at a high temperature circumstance, the heat sensitive recording material being characterized in that 1-phenoxy-2-(2-naphthoxy)ethane and/or 1,3-bis(2-naphthoxy)propane is incorporated in a recording layer.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 97 10 5273

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X,D | US 4 531 140 A (T.SUZUKI ET AL.)<br>* column 1, line 36 - column 2, line 18 *<br>* column 7, line 18; example 1 *<br>* claims 1-5 * | 1-5 | B41M5/30 |
| X | DE 37 03 479 A (FUJI PHOTO FILM COMPANY LIMITED)<br>* page 4, line 55 - page 5, line 49 *<br>* claims 1-10; example 29 * | 1-5 | |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 11, no. 235 (M-612) [2682] , 31 July 1987<br>& JP 62 048587 A (KANZAKI PAPER MANUFACTURING COMPANY LIMITED), 3 March 1987,<br>* abstract * | 1-5 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6)<br>B41M |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 10 June 1997 | Bacon, A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)